(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 359 509
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 89309214.8

(22) Date of filing: 11.09.89

(51) Int. Cl.[5]: C 08 F 226/04
C 08 F 220/56
//(C08F226/04,220:56),
(C08F220/56,226:04)

(30) Priority: 12.09.88 GB 8821310

(43) Date of publication of application:
21.03.90 Bulletin 90/12

(84) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

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(54) Process for the production of high molecular weight copolymers of diallyl dimethyl ammonium chloride and acylamide in solution.

(57) Water-soluble, high molecular weight, linear copolymers of diallyl dimethyl ammonium chloride and acrylamide of various cationicities are prepared by copolymerization of a major portion of the acrylamide monomer via stage-addition in a solvent solution and adding a chain transfer agent at the conclusion of said copolymerization to prevent branching and crosslinking from occurring.

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Description

PROCESS FOR THE PRODUCTION OF HIGH MOLECULAR WEIGHT COPOLYMERS OF DIALLYL DIMETHYL AMMONIUM CHLORIDE AND ACRYLAMIDE IN SOLUTION

This invention relates to high molecular weight, water soluble, linear copolymers of diallyl dimethyl ammonium chloride and acrylamide having varying cationicities, and to methods of preparing the same. Copolymers of this type are useful as cationic flocculants in the treatment of industrial water, as sludge conditioners for the treatment of municipal water systems, and as drainage and retention aids in the manufacture of paper.

Diallyl dimethyl ammonium chloride (DADMAC) is a quaternary monomer, which when polymerized, yields water soluble polymers that are cationic in nature. The polymerization of acrylamide, on the other hand, produces water soluble polymers that are essentially nonionic in nature. Thus, the copolymerization of DADMAC and acrylamide monomers results in the formation of water soluble copolymers having various degrees of cationicity, depending upon the amount of DADMAC that is incorporated into the final copolymer.

The copolymerization of DADMAC and acrylamide monomers in solution is well known. U.S. Patent No. 2,923,701, for example, describes the simultaneous copolymerization of acrylamide and DADMAC in solution by the addition of a redox catalyst, such as ammonium persulfate and potassium metabisulfite, to an aqueous mixture of the monomers.

U.S. Patent No. 3,147,218 discloses the use of DADMAC and acrylamide copolymers for the separation of mineral fines. European Patent Application 103 698 describes the preparation of acrylamide and DADMAC copolymers via the polymerization of a solution of the corresponding monomers in the presence of a free radical initiator. The solvent is removed by polymerizing and drying the resulting polymer solution at a temperature above the boiling point of the solvent.

Copolymers of DADMAC and acrylamide can also be obtained utilizing emulsion polymerization techniques in accordance with the teachings of U.S. Patent No. 3,920,599. Stable water-in-oil copolymer emulsions are prepared, which can then be inverted by means of suitable hydrophilic, water-soluble surfactants. U.S. Patent No. 4,070,930 discloses the preparation of stable emulsion copolymers of DADMAC and acrylamide, which can be inverted by the addition of water. European Patent Application 0 188 721 provides an improved process for the incorporation of DADMAC into an acrylamide polymer by means of either emulsion or solution polymerization techniques. This improvement comprises the step of polymerizing DADMAC and acrylamide in the presence of a copolymerizable monomer, such as a quaternary substituted acrylamide or methacrylamide. The monomer utilized must have a greater reactivity than DADMAC with acrylamide.

The present invention relates to a process for the preparation of high molecular weight, water-soluble, linear copolymer of DADMAC and acrylamide having a uniform DADMAC to acrylamide ratio. More particularly this process comprises the steps of:

a) initiating the copolymerization of a stirred mixture of DADMAC monomer with a portion of the total amount of acrylamide monomer required in a solvent solution at a temperature ranging from 30 to 40°C;

b) adding to said stirred monomer solution the remaining acrylamide monomer via continuous stage addition over a period of from 0.5 to 8 hours at a temperature ranging from 20 to 50°C to form a gel solution;

c) homogeneously mixing a chain transfer agent in said gel solution to form a gel mixture;

d) heating said gel mixture to a temperature of from 60 to 90°C for a a period of from 0.1 to 4 hours;

e) drying said gel mixture, and recovering the desired copolymer therefrom.

This invention also relates to high molecular weight water soluble linear copolymers of DADMAC and acrylamide prepared in accordance with the process of this invention. Such copolymers are particularly useful as flocculants for sludge conditioning in the treatment of municipal and industrial water and waste water systems over a wide range of pH. The copolymers described herein are also useful as drainage and retention aids in the manufacture of paper.

As previously indicated, the preparation of DADMAC and acrylamide copolymers is well known. In general, however, the existing prior art copolymers are non-uniform in their composition and tend to be highly branched and cross-linked. In addition, the prior art copolymers are of relatively low molecular weight, and/or having intrinsic viscosities generally less than 6 dl/g.

The present invention overcomes these deficiencies of the prior art and enables the preparation of high molecular weight copolymers of DADMAC and acrylamide having intrinsic viscosities ranging from 10 to 25 dl/g. More particularly, DADMAC and acrylamide copolymers are prepared in accordance with this invention that have intrinsic viscosities ranging from 15 to 20 dl/g. It is generally recognized by those skilled in the art that intrinsic viscosity is an indication of polymer molecular weight. Thus, the higher the intrinsic viscosity, the greater is the molecular weight of the particular polymer or copolymer prepared.

When prepared in accordance with the teachings of this invention, copolymers of varying cationicities can be prepared. Moreover, such copolymers are uniform in composition. That is to say, copolymers are prepared which contain little, if any, residual monomer, and which have a uniform DADMAC to acrylamide ratio throughout the entire length of the copolymer chain.

One difficulty in the preparation of DADMAC and acrylamide copolymers, having a uniform distribution throughout the length of the copolymer chain, is due to the difference in reactivity of the acrylamide monomer with respect to the DADMAC monomer. This difference in reactivity results in a non-uniform distribution of the DADMAC monomer throughout the copolymer chain. Thus, at the onset of the copolymerization reaction, a relatively larger number of acrylamide monomer units are initially incorporated into the polymer chain due to the greater reactivity of the acrylamide monomer. Accordingly, at the conclusion of the copolymerization reaction, relatively more of the DADMAC monomer units remain unused and remain either as free monomer, or form low molecular weight homopolymers. These excess DADMAC monomers or low molecular weight DADMAC homopolymers remain either as a residual mixture or they become incorporated within the copolymer chain, which results in a non-uniform distribution of copolymer units throughout the copolymer chain. This is particularly true in the case of copolymers wherein the final DADMAC content is greater than 20 percent on a molar basis of the total copolymer content.

A further difficulty in the preparation of high molecular weight linear copolymers of DADMAC and acrylamide is due to the manner in which the DADMAC monomer polymerizes. Normally, the DADMAC monomer polymerizes by incorporating both of the allyl bonds within the same molecule to form a linear polymer chain. A small proportion of the DADMAC monomer, however, can polymerize via the incorporation of only one of its allyl bonds, thereby leaving a pendant double bond remaining in the molecule. These pendant double bonds can subsequently initiate branching, particularly at higher temperatures, to produce cross-linked polymers that have a reduced solubility in water, see Jaeger et al., Journal of Macromolecular Science, Part A Chemistry, 593-614, (1984).

This greater reactivity of the acrylamide monomer in combination with the tendency of the DADMAC monomer to polymerize via branching or cross-linking, results in the formation of non-linear DADMAC and acrylamide copolymers having relatively low intrinsic viscosities, and which are not particularly well suited as flocculants in water and waste water systems for sludge conditioning, or as drainage and retention aids in the manufacture of paper. These problems have been overcome by means of the present invention, which enables the preparation of high molecular weight, linear copolymers of DADMAC and acrylamide of uniform composition that have little, if any, branching and cross-linking in the polymer chain.

In general, the process of this invention essentially utilizes a controlled addition or stage-addition of the acrylamide monomer during the copolymerization reaction. Surprisingly, it has been discovered that this continuous stage-addition of the acrylamide monomer produces high molecular weight copolymers of DADMAC and acrylamide which heretofore have not, as yet, been available. Additionally, copolymers having high DADMAC conversions can be prepared that contain a uniform distribution of DADMAC and acrylamide monomer units throughout the entire length of the copolymer chain with little, if any, residual DADMAC or acrylamide monomer remaining in the finished product. In addition, the process of this invention also utilizes the addition of a chain transfer agent to prevent branching and cross-linking of the polymer chain from occurring, paticularly at elevated temperatures.

To initiate copolymerization, a portion of the acrylamide monomer is added to the total amount of DADMAC monomer that is required. In general, about 12 to 20 percent of the total amount of acrylamide is initially added to the reaction mixture. More particularly, from 15 to 17 percent of the total amount of acrylamide monomer required is generally added to initiate copolymerization. The copolymerization reaction of DADMAC and acrylamide is an exothermic reaction. Thus, once copolymerization begins, the temperature of the reaction mixture rapidly increases. At this point the remaining amount of acrylamide monomer is introduced to the reaction mixture via a process of stage-addition. After all of the acrylamide monomer has been stage-added to the reaction mixture, a chain transfer agent is added in order to prevent any branching or cross-linking of the polymer chain from occurring.

The copolymerization reaction is conducted in solution in the presence of a suitable solvent. Suitable solvents include water, primary alcohols having from 1 to 4 carbon atoms, and aqueous mixtures thereof. The use of lower alcohols has the advantage that it can provide a granular product that is easier to handle and that can be more readily dried. However, inasmuch as both the starting materials and final products are soluble in water, water is generally the solvent of choice.

Sufficient water should be employed to facilitate polymerization and to homogeneously dissolve all of the components of the reaction mixture. Aqueous monomer solutions containing from 40 to 70 percent of monomer can advantageously be employed as starting solutions. Preferably, aqueous monomer solutions containing from 50 to 60 percent monomer are generally employed. If necessary, additional water can be added to the reaction mixture during the course of the reaction in order to provide optimum conditions for polymerization and adequate mixing.

One important aspect of this invention is that copolymers of varying cationicities can be precisely prepared in accordance with the process of this invention. The greater the number of DADMAC units introduced into the polymer chain, the greater will be the cationicity of the resulting copolymer. Thus, copolymers useful as cationic flocculants in water clarification systems or as sewage dewatering agents, require copolymers having a higher degree of cationicity than cationic flocculants useful as drainage and/or retention aids in the manufacture of paper. The copolymers contemplated by the present invention range from 5 to 95 mole percent cationicity. That is to say, in a copolymer consisting of 100 monomer units, the copolymers described herein comprise from about 5 to 95 DADMAC monomer units, and conversely from about 95 to 5 acrylamide monomer units. Preferably, copolymers comprising from about 5 to 75 mole percent cationicity can be prepared. Still more preferably, polymers having from 10 to 50 mole percent cationicity can be prepared in accordance with the teachings of this invention.

The period of time during which stage addition occurs is dependant upon the amount of DADMAC monomer units that are to be introduced into the polymer chain. Thus a copolymer having a 10 mole percent cationicity requires approximately one hour of stage addition, whereas a copolymer having 30 mole percent cationicity requires approximately 3 hours for stage addition to take place. Copolymers having up to 90 mole percent cationicity require approximately 8 hours for stage addition to take place. These periods of time will, of course, vary slightly depending upon the type and design of reactor employed, the degree of mixing and the temperature at which the copolymerization is conducted. For large scale preparations, the particular parameters to be employed can be optimized via standard procedures known to those skilled in the art.

The stage-added acrylamide monomer solution is continuously introduced in such a manner that a slightly decreasing feed rate is achieved throughout the total period of stage addition. Thus, for example, during the first quarter of the period for stage addition, approximately 30 to 35 percent of the acrylamide monomer solution is stage-added; during the second quarter of the stage-addition period, 25 to 30 percent of the acrylamide monomer solution is stage-added; during the third quarter about 20 to 25 percent of the monomer solution is stage-added; and the final 15 to 20 percent of the acrylamide monomer solution is introduced during the final quarter of the stage addition period. For the production of large quantities of copolymers, a metering pump can be advantageously employed.

The copolymerization reaction is generally initiated using free radical polymerization techniques known to those skilled in the art. Compounds which form mainly water soluble radicals are suitable as polymerization initiators. For example, azostarters such as 2,2-azobis-(N,N′-dimethylene-isobutyramidine) dihydrochloride, 2,2′-azobis-(2-amidinopropane) dihydrochloride, 2,2′-azobis-(N,N′dimethylene-isobutyramidine), 4,4′-azobis-(4-cyanopentane-carboxylic acid), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2′-azobis(2,4-dimethyl-valeronitrile), (1-Phenylethyl)azodiphenylmethane, 2,2′-azobisisobutyronitrile, dimethyl 2,2′-azobisisobutyrate, and 2,2′-azobis-(2-methyl-butyronitrile) can be employed.

Additionally, peroxide polymerization initiators can be employed, as for example, dibenzoyl peroxide, dilauryl peroxide, di-2-ethylhexylperoxydicarbonate, dicyclohexylperoxydicarbonate, bis-(4-tert butylcyclohexyl)peroxydicarbonate, tert. butylperpivalate, tert. butyl-perbenzoate, tert. butylpermaleinate, di-tert. butyl-peroxide, tert.-butylhydroperoxide, hydrogen peroxide, ammonium persulfate, potassium persulfate, sodium persulfate, and redox catalysts in combination with reducing agents such as iron(II)-ammonium sulfate, ascorbic acid, sodium methyl sulfinate, disodium disulfite and sodium hydrogen sulfite can be employed. These initiators can be used either alone or in combination with one another.

The rate of decomposition of the more readily decomposed peroxides can be reduced by the addition of organic metal complex compounds, as for example, copper acetyl acetonate. Thus the rate of peroxide decomposition can be adapted, for example, to the particular polymerization temperature selected. Preferred redox catalysts are those selected from one or several peroxides in combination with a reducing agent. Especially preferred are persulfates or peresters or mixtures of persulfates and peresters as a component of the redox polymerization initiators. The polymerization initiators are used in amounts ranging from 0.001 to 5 percent by weight, and preferably from about 0.02 to 2 percent by weight, relating to the amount of monomers utilized.

It is very important to keep the reaction mixture well mixed and in intimate contact with the stage-added acrylamide monomer throughout the entire stage-addition process, in order to obtain a homogeneous distribution of DADMAC throughout the copolymer chain. Insufficient mixing results in a non-homogenous polymerization, whereas too rapid or too intensive mixing results in polymer degradation. Adequate mixing of the copolymerization mixture is of particular importance in the latter stages of the copolymerization due to the gel which forms.

The degree and amount of mixing required to homogeneously blend the reaction mixture varies widely depending upon the size and the shape of the particular apparatus employed. Reaction mixers used in the preparation of gels or other similar materials, that provide intimate mixing and kneading via a shearing action, are particularly well suited to this process. During the latter stages of polymerization a gel solution forms which becomes progressively more and more viscous. This gel solution may require additional water as well as additional mixing time in order to obtain a homogenous reaction mixture.

The optimum temperature at which polymerization occurs ranges from 20 to 50°C. Preferably, polymerization is conducted at a temperature ranging from 30 to 40°C. Still more preferably a temperature of 35°C is employed. Copolymers of DADMAC and acrylamide prepared at a temperature of 35°C are completely soluble in water, irregardless of how large their molecular weights are. On the other hand, copolymers prepared at temperatures above 40°C tend to be insoluble or partially soluble. This insolubility is the result of the increased tendency for the DADMAC monomer to polymerize via branching and cross-linking at higher temperatures. The more branched and cross-linked the copolymers become, the less soluble they are in water. Indeed, one of the qualitative tests for the degree of branching and cross-linking for this type of copolymer is its solubility in water.

Inasmuch as the polymerization reaction is exothermic in nature, control of the reaction temperature is critical. In order to maintain close control over the reaction temperature, the boiling point of the particular reaction solvent mixture is utilized. Thus, where water is employed as the reaction solvent, the reaction is conducted under a reduced pressure ranging from 35 to 60 millibars, preferably from 50 to 55 millibars pressure, in order to maintain a constant temperature of 35 ± 1.0°C. Following the stage addition of all of the acrylamide monomer solution, the reaction mixture preferably is stirred for an additional 30 minutes to 1 hour at a temperature of 35°C in order to complete polymerization.

After the completion of the polymerization reaction, the reaction vessel is brought to atmospheric pressure utilizing nitrogen or some other inert gas. A polymerization reaction regulator or chain transfer agent is added to the gel solution with mixing in order to prevent branching and cross-linking from occurring. Suitable chain transfer agents include, for example, lower alkyl alcohols having from 1 to 5 carbon atoms, mercaptoethanol, mercaptopropanol, thioglycolic acid, dodecylmercaptan, formic acid, halogenated hydrocarbons, such as bromoethane or carbon tetrachloride, and sodium hypophosphite. Preferably, a solution of sodium hypophosphite is employed. The chain transfer agents are used in amounts ranging from 0 to 3 percent by weight with respect to the monomers employed and must be thoroughly mixed with the gel mixture.

Following the addition of the chain transfer agent, the reaction mixture is heated to 75°C and maintained at that temperature for a period of from 0.1 to 4.0 hours. This period of heating serves to minimize the residual monomer content of the copolymer produced. This is especially important with respect to any residual acrylamide monomer that may be present, so that copolymers are prepared that are environmentally compatible.

The gel mixture containing the desired product is cooled, discharged from the reactor and dried. Alternatively, prior to drying, the gel mixture can be extruded and granulated in order to assist the final drying step. The product so prepared can be dried using any well known means for drying, as for example, a fluidized bed, a circulating air conveyer, vacuum drying or microwave drying. The dried product is obtained as a white, granular, pourable material, which is completely soluble in water, and which has an intrinsic viscosity, as determined by viscosity measurements in a 4 percent sodium chloride solution, ranging from 10 to 25 dl/g.

The following methods can be used to qualitatively and quantitatively determine the degree of DADMAC monomer incorporation into the final copolymer.

(1) Solubility in Methanol

Copolymers of DADMAC and acrylamide having a DADMAC content greater than 30 mole percent are soluble in methanol. Copolymers in the range of 30 mole percent are soluble in methanol, if, in addition, the methanol contains 10 to 20 percent water. Copolymers of low DADMAC content, as well as the homopolymer of acrylamide are totally insoluble in methanol or mixtures of 80 percent methanol and 20 percent water. The fact that the 50 mole percent copolymer of Example 4 and the 30 mole percent copolymer of Example 3 are soluble in methanol and a methanol-water mixture (80 percent / 20 percent), respectively, demonstrates that no homopolyacrylamides or copolymers of low DADMAC content are present in these copolymers.

(2) Colloidal Titration Using Potassium Polyvinyl Sulfate

Using the method described by W Schempp et al., Papier, 36 (10A), 41-6 (1982), the cationicity of the various copolymers produced can be determined. This procedure provides a method for determining the cationic charges bound to the particular polymer tested as expressed in eq/kg. Comparison with the theoretical calculated values, enables the calculation of the degree of DADMAC conversion.

The copolymers produced in accordance with this invention are used as aids in the dewatering of a wide variety of aqueous suspensions. These copolymers are particularly useful in the dewatering of organic sludge suspensions that are proteinaceous in nature or the dewatering of suspensions that have been obtained by the biological degradation of such matter. Such suspensions can be derived from raw or processed sewage, food waste, and fermentation effluents. The copolymers of this invention are also useful in the clarification of various types of industrial waste waters.

It is frequently desirable to dewater such sludges or suspensions in order to facilitate their removal and their disposal. Dewatering can be effected by the addition of an appropriate amount of the copolymer as a flocculanting agent prior to the physical removal of water. Dewatering of sludges or suspensions is usually effected by the addition of an aqueous solution of the polymer having a concentration ranging from 0.01 to 1 percent by weight of polymer. Preferably from 0.05 percent to 0.5 percent of copolymer solution is employed. Typical addition rates for sewage sludge are in the range 0.2 to 1.0 percent of polymer per total weight of sewage solids.

The copolymers of this invention are also useful in the paper industry as drainage and retention aids in the manufacture of paper, and in the dewatering of aqueous effluents containing cellulosic fibers. Such uses include, for example, treating aqueous waste water from a paper mill prior to discharge of the effluent, or treating return process water for the papermaking process. Such water may contain suspensions of cellulose or other finely divided particles in concentrations ranging from 50 ppm to 1 or 2 percent by weight of solution. The copolymers of this invention are particlarly useful and are generally employed as 0.01 to 1 percent solutions. However, it is sometimes more convenient to prepare 1 to 2 percent stock solutions, from which the copolymers can be utilized.

The invention described and claimed herein is more particularly illustrated in conjunction with the following examples, which are not intended to limit the invention in any way.

Example 1

To 2.89 kg of a 60 percent aqueous solution of DADMAC is added 2.11 kg of a 50 percent aqueous solution of acrylamide, 3.31 kg of water, 27 g of a 40 percent aqueous solution of the pentasodium salt of diethylenetriaminepentaacetic acid, 2g of 2,2-azobis(N,N'dimethyleneisobutyramidine) dihydrochloride, 5g of

2,2′-azobis(2-amidinopropane) dihydrochloride, and 27 g of sodium persulfate in a 30 liter horizontal reaction vessel equipped with a mixing shaft, heating jacket, vacuum control, reflux condenser and inlet ports for stage addition. The reaction mixture is deoxygenated by repeatedly evacuating the system and purging it with nitrogen. This process is repeated two additional times to insure complete deoxygenation.

The reaction mixture is heated with stirring to initiate polymerization. Once polymerization begins, the reaction is evacuated to 50-55 millibars in order to maintain a close temperature control of the exothermic reaction. As soon as an increase in temperature is observed, the remaining 11.62 kg of a 50 percent aqueous solution of acrylamide, and an additional 3.0g of 2,2′-azobis (N,N′-dimethyleneisobutyramidine) dihydrochloride in water is added over a period of one hour, via stage-addition, with constant stirring. The feed rate is adjusted so that approximately 29 percent of the acrylamide solution is added during the first quarter of the total time period, 26 percent is added during the second quarter, 24 percent during the third quarter, and the remaining 21 percent of the acrylamide solution is added during the last quarter of the total time period of one hour.

After all of the acrylamide monomer solution has been stage-added, the reaction mixture is stirred for an additional 40 minutes while maintaining the reaction temperature at 35°C. The reaction vessel is brought to atmospheric pressure with nitrogen and 0.5 kg of a 10 percent aqueous sodium hypophosphite solution is added to the gel solution over a 30 minute period, taking care to mix the sodium hypophosphite solution carefully into the gel mixture. The temperature of the reaction mixture is raised to 75°C and maintained for a period of 2 hours to effectively reduce any residual monomer that remains.

The gel mixture is discharged into a simple granulator and dried in a fluid bed drier at 90°C for 50 minutes to produce a dry, white granular copolymer comprising 10 mole percent cationicity and having a uniform distribution throughout the polymer chain. This copolymer has an intrinsic viscosity of 16 dl/g when measured in 4 percent sodium chloride solution at 25°C using a Brookfield LVT with a UL adapter. The actual cationicity as determined by potassium polyvinyl sulfate titration shows a cationicity of 1.24 eq/kg as compared to a theoretical cationicity of 1.25 eq/kg (99 percent DADMAC conversion). The copolymer is soluble in water and insoluble in methanol.

Examples 2-4

Following essentially the same procedure as in Example 1, but making the equivalent substitutions shown below, copolymers of varying cationicities are obtained. All weights are expressed in kg.

Example	2	3	4
Initial DADMAC charge (60 % solution)	4.33	7.57	11.57
Initial Acrylamide charge (50 % solution)	1.87	1.56	1.08
Water	3.60	3.05	1.98
Pentasodium salt of diethylenetriamine-pentacetic acid (40 % solution)	0.023	0.023	0.022
2,2′azobis-(2-amidine-propane)-dihydrochloride	0.005	0.005	0.005
Sodium persulfate	0.027	0.027	0.027
2,2′-azobis(N,N-dimethylene-isobutyramidine) dihydrochloride	0.002	0.002	0.002
Stage addition-50 % acrylamide solution	10.13	7.75	5.30
Stage addition-2,2′-azobis-(N,N′-dimethylene-isobutyramidine) dihydrochloride	0.003	0.003	0.003
Sodium hypophosphite (10 % solution)	0.5	0.5	0.5
Reaction Temperature (°C)	35	35	35
Stage Addition (hrs)	2	3	4
pH of reaction mixture	7	7	7

The copolymers of DADMAC and acrylamide so obtained have the following properties:

Example	2	3	4
Cationicity (mole %)	16	30	50
Cationic Titration (eq/kg)			
Theoretical	1.87	3.05	4.3
Actual	1.73	2.6	3.8
DADMAC Conversion (%)	92.5	85	89.3
*Intrinsic Viscosity (dl/g)	12.8	12.5	13.3
Solubility Water	sol	sol	sol
Solubility Methanol	insol	**insol	sol

* 4 % NaCl at 25°C
** Sol 80 % methanol / 20 % water

Comparative Examples 5-8

Following essentially the same procedures described in Examples 1-4, but without the stage adding of the acrylamide monomer, copolymers having the following properties were obtained.

Example	5	6	7	8
Cationicity (mole %)	10	16	30	50
Cationic Titration (eq/kg)				
Theoretical	1.25	1.87	3.05	4.3
Actual	0.40	0.67	1.37	2.09
DADMAC Conversion (%)	32	36.1	45	48.7

As evidenced by the poor rates of DADMAC conversion and corresponding lack of cationicity, these non-uniform copolymers of DADMAC and acrylamide are unsuitable as flocculants for sludge conditioning in the treatment of municipal and industrial water waste systems.

Example 9

Following essentially the same procedure described in Examples 1-4, but omitting the use of sodium hypophosphite as a chain transfer agent, crosslinked DADMAC and acrylamide copolymers are obtained which are insoluble in water. Such copolymers are not suitable for use as flocculating agents, due to their lack of solubility.

Claims

1. A process for the preparation of a water-soluble, linear copolymer of diallyl dimethyl ammonium chloride (DADMAC) and acrylamide having a uniform DADMAC to acrylamide ratio comprising the steps of:

(a) initiating the copolymerization of a stirred mixture of DADMAC monomer by heating with a portion of the total amount of acrylamide monomer required in a solvent solution;

(b) adding to said stirred monomer solution the remaining acrylamide monomer by continuous addition to form a homogeneous gel solution;

(c) homogenously mixing a chain transfer agent in said gel solution to form a gel mixture;

(d) heating said gel mixture to minimize residual monomer content; and

(e) drying said gel mixture.

2. A process as claimed in Claim 1, wherein the solvent is water or C_1-C_4 primary alcohol.

3. A process as claimed in Claim 1 or Claim 2, wherein the polymerization temperature is 30 to 40° C.

4. A process as claimed in any one of the preceding claims, wherein 15 to 17 percent of the total amount of acrylamide monomer is added to step (a).

5. A process as claimed in any one of the preceding claims, wherein the addition of the said remaining acrylamide in step (b) is over a period of 0.5 to 8 hours at a temperature of 20 to 50° C.

6. A process as claimed in any one of the preceding claims, wherein the said remaining acrylamide is added in such a manner that a decreasing feed rate is achieved over the period of addition.

7. A process as claimed in Claim 6, wherein 30 to 35 percent of the acrylamide is added during the first quarter of the said addition period, 25 to 30 percent is added during the second quarter, 20 to 25 percent is added during the third quarter, and 15 to 20 percent is added during the final quarter.

8. A process as claimed in any one of the preceding claims, wherein the chain transfer agent is sodium hypophosphite.

9. A process as claimed in any one of the preceding claims, wherein the heating of step (d) is conducted at 60 to 90° C for 0.1 to 4.0 hours.

10. A process as claimed in any one of the preceding claims, wherein DADMAC to acrylamide ratio is from 5 to 15 mole percent.

11. A process as claimed in any one of Claims 1 to 9, wherein the DADMAC to acrylamide ratio is from 25 to 50 mole percent.

12. A water-soluble, linear copolymer of diallyl dimethyl ammonium chloride (DADMAC) and acrylamide having a uniform DADMAC to acrylamide ratio and an intrinsic viscosity of from 10 to 25 dl/g as determined in a 4 percent sodium chloride solution.

13. A copolymer as claimed in Claim 12, wherein said intrinsic viscosity is from 15 to 20 dl/g.

14. The use of a copolymer as claimed in Claim 12 or Claim 13 as a flocculant for aqueous suspension.

15. The use of a copolymer as claimed in Claim 12 or Claim 13 as a drainage or retention aid in paper manufacture.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 9214

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 585 148 (J.J. SACKIS) * Claim 1; example 1 * ---	1-13	C 08 F 226/04 C 08 F 220/56 // (C 08 F 226/04 C 08 F 220:56) (C 08 F 220/56 C 08 F 226:04)
D,A	EP-A-0 247 774 (EXXON CHEM. PAT.) * Claim 16 * -----	14-15	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-11-1989	CAUWENBERG C.L.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document